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FULL PAPER

Fe_3O_4@APTES@isatin-SO_3H as heterogeneous and efficient catalyst for the synthesis of quinoxaline derivatives

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In this work, an efficient and new Fe_3O_4@APTES@isatin-$SO_3H$was synthesized through immobilization of isatin sulfonic acid on silica modified Fe_3O_4 nanoparticles. The synthesizedFe_3O_4@APTES@isatin-SO_3Hmagnetic nanoparticles (MNPs) were characterized using the energy dispersive X-ray spectroscopy (EDX), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), vibrating sample magnetometer (VSM), X-ray diffraction (XRD), and thermogravimetric(TGA) analysis. The Fe_3O_4@APTES@isatin-SO_3HMNPs performed efficient catalytic activity as a magnetically recyclable heterogeneous catalyst for one-pot, condensation reaction of 1,2-dicarbonyl compounds and o-phenylen diamines in ethanol at room temperature to afford quinoxaline derivatives.

KEYWORDS

Fe_3O_4@APTES@isatin-SO_3H; quinoxaline, *O*-phenylen diamines; 1, 2-dicarbonyl; nanocatalyst.

Introduction

Recently, the chemists have greatly focused on developing the eco-friendly catalysts and methods in the synthetic organic material and industrial fields [1, 2].Over the last few decades, a growing research interest has been directed towards the preparation and application of highly efficient and recyclable catalysts in the modern synthetic processes [3-6].Magnetic Fe_3O_4 nanoparticles have emerged as privileged support for immobilization of various functional groups such as phosphorous, nitrogen and organic moieties owing to the presence of high density hydroxyl groups on their surface, high surface area, high stability, facile magnetic separation, environmental benignity and high loading capacity [7-18]. Among the heterocyclic compounds, quinoxaline and derivatives are the most important compounds due to their biological and pharmacological properties which perform antifungal [19], insecticide [20], antibacterial [21], anticancer, antimalarial, anti-HIV[22] and antibiotics[23] activities. In addition, quinoxaline derivatives are used in industry, in dyes, fluorescent dyes, materials having electroluminescence properties and in the synthesis of organic semiconductors [24]. The methods reported in the literature for the synthesis of quinoxaline utilize various catalytic systems such as ultrasonic[25], $CuSO_4.5H_2O$ (II) [26], catalyst-free [27], Si/MCM-41 [28], phosphor sulfonic acid [29], boron sulfonic acid [30], $(NH_4)_6Mo_7O_{24}.4H_2O$[31], bismuth (III) triflate[32], ammonium chloride [33], and Zn(L-proline) [34].

Following our recent attempt in the development of efficient and heterogeneous catalysts for organic synthesis of various

heterocyclic compounds including the quinoxaline[30],we report the synthesis of isatin sulfonic acid immobilized on core-shell on silica modified Fe_3O_4 nanoparticles, and its application as a new versatile and recyclable heterogeneous nanocatalyst for the synthesis of quinoxaline derivatives *via* condensation reactions between 1,2-dicarbonyl and *o*-phenylen diamines in ethanol at room temperature to afford quinoxaline derivatives.

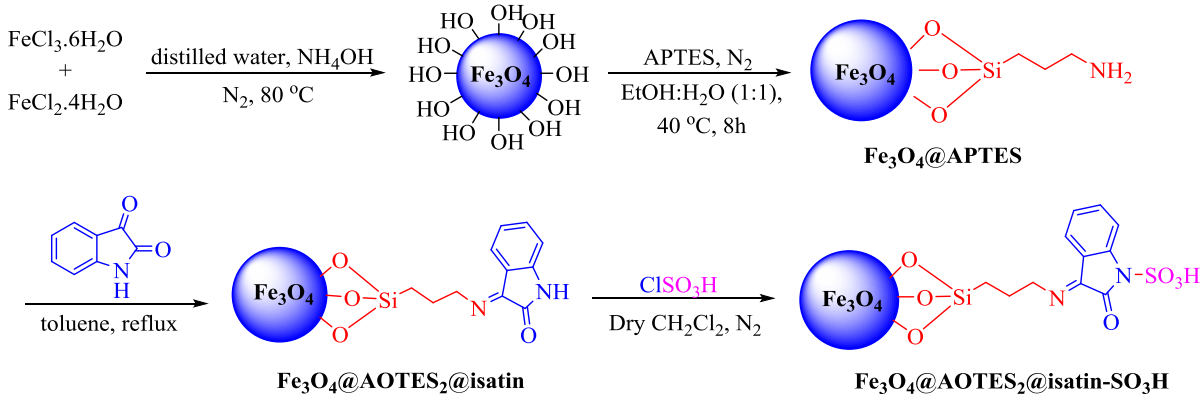
Experimental

General

The solvents and chemicals utilized in this research study were purchased from the Merck Chemical Company and used without further purification. Melting points were determined in open capillary tubes using a Shimadzu 435-U-04. Fourier transform infrared (FT-IR) spectra were recorded from KBr pellets on a Perkin Elmer GX FT-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded for samples in $CDCl_3$ or DMSO-d_6 on 90 MHz BRUKER AVANCE instruments at ambient temperature using tetramethylsilane (TMS) as internal standard. Microstructure of the material was assessed using the scanning electron microscopy (SEM, model EM3200,operated at 30 kV accelerating voltage). Energy-dispersive X-ray (EDX) analysis was carried out using a FESEM-SIGM (German) instrument. The curves obtained from thermo-gravimetric analysis (TGA) were recorded in air using TGA/DTA PYRIS DIAMOND instrument. Magnetic measurement of the catalyst was performed using a vibrating sample magnetometer (VSM) instrument MDKFT. Moreover, high resolution transmission electron microscopy (TEM) was conducted on the nanoparticles using a HRTEM Philips CM30, (300KV) instrument.

Preparation of Fe_3O_4@APTES@isatin-SO_3H

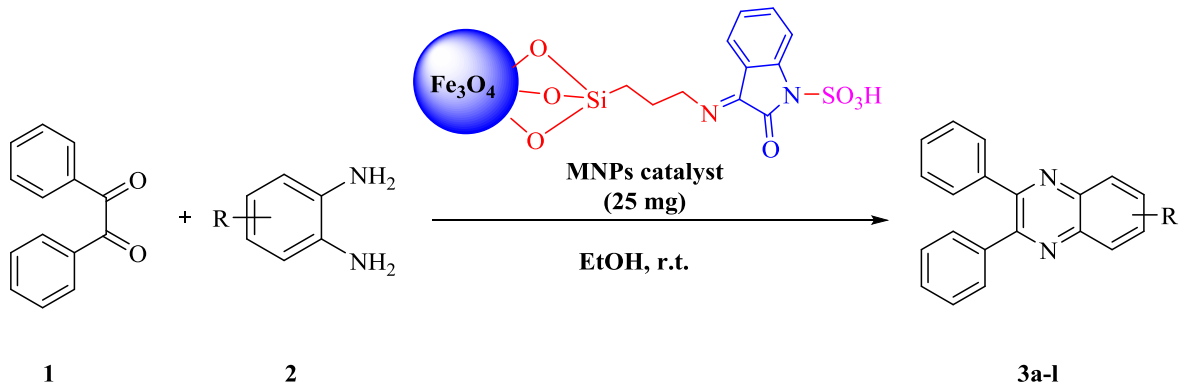
Magnetite Fe_3O_4@APTES@isatin-SO_3H was prepared according to the literature procedure and fully characterized by EDX, FT-IR, XRD, VSM, TEM, SEM, and TGA techniques (Please see supporting information [35].



SCHEME 1 Synthesis of Fe_3O_4 magnetic nanoparticles

Synthesis of quinoxaline derivatives

In a 20 mL round bottom balloon, a mixture of ortho-phenylene diamine (1 mmol) and 1, 2-dicarbonyl (1 mmol) in the presence of magnetic catalysts (25 mg) in 5 mL of ethanol as solvent at the room temperature was stirred. The reaction progress was monitored by thin layer chromatography (TLC). The reaction continued until the completion of reaction. Upon completion of the reaction, the catalyst was separated by applying an external magnetic field, and the pure product was obtained by recrystallization with hot ethanol and then the product was recovered with high efficiency (Scheme 2, Table 2).



SCHEME 2 Synthesis of quinoxaline derivatives at room temperature using Fe_3O_4@APTES@isatin-SO_3H nanocatalyst

Selected Data

*Diphenylquinoxaline(**3a**)*

White solid,^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.3 (bs, 6H, Ar-H), 7.5 (bs, 4H, Ar-H), 7.7 (bs, 2H, Ar-H), 8.2 (bs, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 128.2, 128.8, 129.1, 129.9, 130, 138.9, 141.1, 153.3.

*Dibenzo[a, c]phenazine(**3b**)*

Yellow solid, ^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.71 (s, 4H, Ar-H), 7.85 (s, 2H, Ar-H), 8.35 (s, 2H, Ar-H), 8.43 (s, 2H, Ar-H), 9.33 (s, 2H, Ar-H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 122.8, 126.4, 128, 128.9, 129.3, 130.2, 130.6, 132, 141.3.

Results and discussion

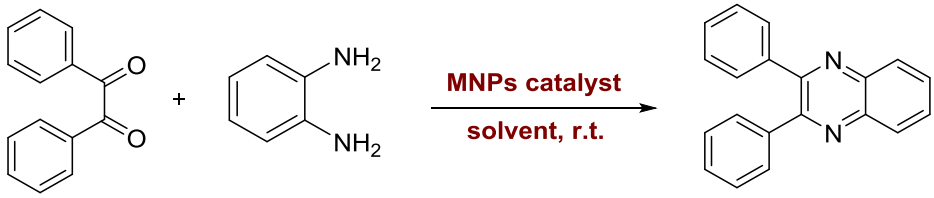
Characterization of the Fe_3O_4@APTES@isatin-SO_3H nanocatalyst

Initially, Fe_3O_4@APTES@isatin-SO_3H as a heterogeneous Brønsted acidic nanocatalyst were prepared according to literatures in Scheme 1, and then shape, size, and morphology fully characterized by a series of EDX, FT-IR, XRD, VSM, TEM, SEM, and TGA analysis techniques (Experimental details were provided in the supplementary data)[35].

Catalyst activity of Fe_3O_4@APTES@isatin-SO_3H

To evaluate the catalytic activity of the synthesized Fe_3O_4@APTES@isatin-SO_3Hnanoparticles, we evaluated the condensation reactions between the diphenyl ketone and o-phenylen diamine using Fe_3O_4@APTES@isatin-SO_3Hnanoparticles as the catalyst in ethanol at room temperature. At the first step, the effects of different reaction parameters such as catalyst loading, solvent, and temperature on the reaction were screened using the reaction between *o*-phenyl diamine (1 mmol) and benzyl (1 mmol)as the model reaction. The mixture of water and ethanol, methanol, ethyl acetate, dichloromethane and chloroform at room temperature was considered. The results of this study are shown in Table 1. As the results show, 25 mg of the catalyst and ethanol solvent are the best conditions for these reactions (Table 1, Entry 6) and the addition of the catalyst does not significantly improve the reaction process.

TABLE 1 Optimization for the reaction of *o*-phenyl diamine and benzyl as model reaction at room temperature

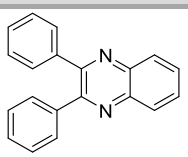
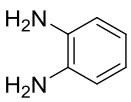
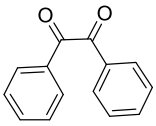
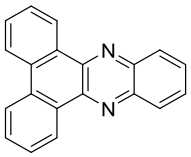
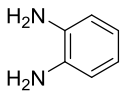
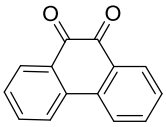
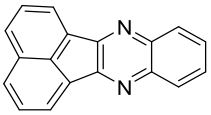
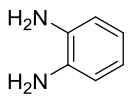
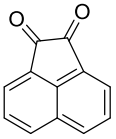
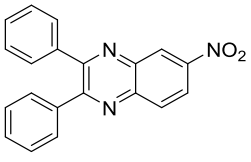
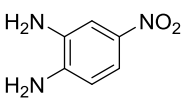
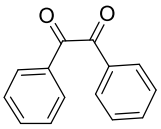


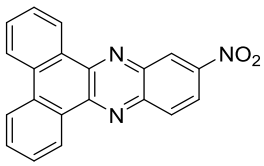
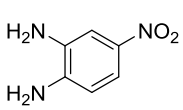
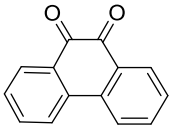
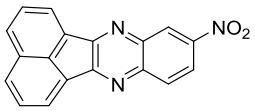
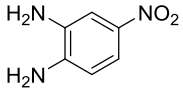
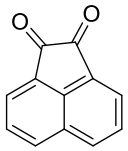
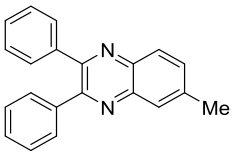
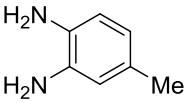
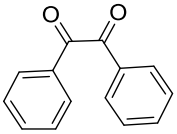
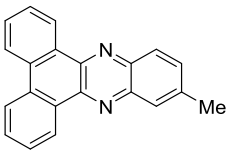
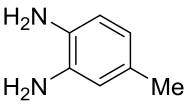
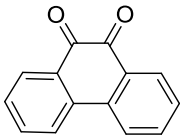
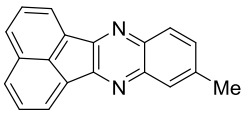
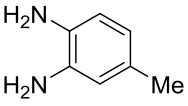
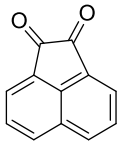
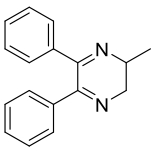
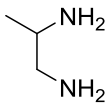
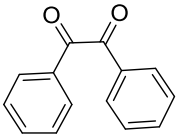
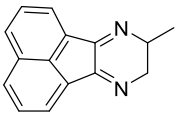
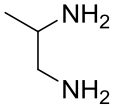
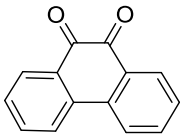
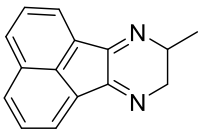
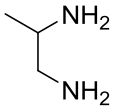
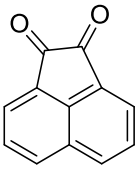
Entry	Amount of catalyst (mg)	Solvent (5 mL)	Time (min)	Yield (%)[a]
1	5	EtOH	90	89
2	7	EtOH	65	91
3	10	EtOH	50	94
4	15	EtOH	35	94
5	20	EtOH	25	95
6	25	EtOH	20	95
7	30	EtOH	20	93
8	25	MeOH	60	65
9	25	EtOAc	60	65
10	25	CH_2Cl_2	60	70
11	25	$CHCl_3$	60	65
12	25	EtOH:H_2O (1:1)	40	75

[a]Isolated yields

With the optimized reaction conditions in hand, various 1,2-dicarbonyl compounds including, benzil, phenanthrene-9,10-dione, and acenaphthylene-1,2-dione were reacted with o-phenylen diamines with electron-releasing substituents and electron-withdrawing substituents to furnish the corresponding products (Table 2). Besides, in all cases, regardless of the nature of the substituent, the reactions gave the products in good to high yields during short reaction times.

TABLE 2 Synthesis of quinoxaline derivatives using Fe_3O_4@APTES@isatin-SO_3H

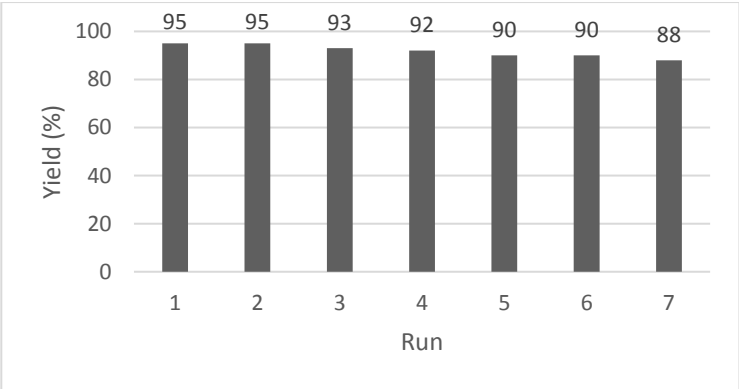
Entry	product	diamine	diketone	Time (min)	Yield (%)[a]	m.p. [Ref]
1				20	95	128-130[36]
2				20	94	225-227[36]
3				25	96	234-236[36]
4				70	95	192-193[36]

5				60	93	186-189[36]
6				60	92	217-219[36]
7				15	94	117-119[36]
8				17	96	234-236[36]
9				15	92	220-221[36]
10				30	90	122-123[36]
11				25	88	179-181[36]
12				30	85	115-117[36]

[a]Isolated yields

Catalyst Recyclability

We studied the recycling and reusability of the Fe_3O_4@APTES@isatin-SO_3H catalyst for the model reaction between *o*-phenlene diamine and benzyl under the optimized conditions. After completion of the reaction, the catalyst was separated magnetically using a magnet. The isolated nanoparticles were washed with ethanol and water several times, oven-dried at 60 ˚C, and reused for seven successive runs with no significant loss of activity (Figure 1).



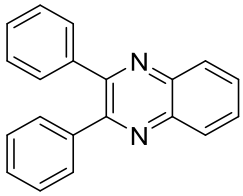


FIGURE 1 Recovery of Fe_3O_4@APTES@isatin-SO_3Hcatalyst in the reaction of o-phenyl diamine and benzyl as model at room temperature

In follow, the other catalysts used for the synthesis of quinoxaline were compared with the present method (temperature, solvent and catalyst), and the results are summarized in Table 3.

TABLE 3 Comparison of other catalysts for the synthesis of quinoxaline derivatives

Entry	Catalyst	Reaction condition	Yield (%)	Ref.
1	-	Solvent free / 130-100 °C / Microwave	84-98	37
2	Alumina	90 °C / solvent free	45-96	38
3	NH_4Cl	Methanol / room temperature	20-100	33
4	Zn(L-proline)	Acetic acid / room temperature / pressure	92-96	34
5	$HClO_4/SiO_2$	Acetonitrile / at room temperature	70-95	39
6	Betacyclo Dextrin	H_2O/ 70 °C	83-92	40
7	$Yb(OTf)_3$	Solvent-free	78-93	41
8	I_2	Dimethyl sulfoxide / room temperature	85-95	42
9	Present work	Room temperature / ethanol	85-96	-

Conclusion

In the present research, we report the synthesis of the quinoxaline derivatives Fe_3O_4@APTES@isatin-SO_3Hcatalyst. The catalyst was structurally investigated using the FT-IR, SEM, TEM, EDX, XRD, TGA, and VSM analytical techniques. The synthesized nanoparticles were explored as efficient heterogeneous Lewis acid catalyst for the synthesis of various quinoxaline derivatives *via* one-pot condensation reactions between 1,2-dicarbonyl and *o*-phenylen diamines in ethanol at room temperature. Moreover, this catalyst can be easily recycled and reused for seven times without significant loss of catalytic activity.

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